

Contributions to the Chemistry of Copper; by T. STERRY
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§ 1. THE resemblances between silver and copper in its cuprous form have already attracted the attention of chemists. The ordinary chlorid of silver (argentic chlorid) and the dichlorid of copper (cuprous chlorid) have many properties in common. Both of these chlorids are white, readily fusible, and blackened by exposure to light; both of them are insoluble in water but dissolve in ammonia and in aqueous solutions of other chlorids, in which however the cuprous is far more soluble than the argentic chlorid. A saturated solution of chlorid of sodium holds at 90° Centigrade, 16.9 per cent of cuprous chlorid, at 40° C., 11.7, and at 11°, 8.9 per cent. A solution containing fifteen per cent of chlorid of sodium retains at 90° C., 10.3 per cent of cuprous chlorid, at 40°, 6.9 per cent, and at 14°, 3.6 per cent; while a solution with only five per cent of chlorid of sodium holds of the cuprous chlorid at 90°, 2.6, and at 40° only 1.1 per cent. These determinations are from single observations and therefore require verification. From the sparing solubility of the cuprous chlorid in dilute solutions of chlorid of sodium it follows that the denser saturated solutions are copiously precipitated by dilution with water, which causes the separation of white cuprous chlorid in a crystalline condition.

§ 2. The aqueous solutions of the chlorids of calcium, magnesium, zinc, manganese, cobalt, ferrous and cupricum, also freely dissolve cuprous chlorid, and it is probable that this property is shared by other soluble chlorids. The strong affinity of cuprous for chlorine enables cuprous oxyd to decompose all the chlorids just named, with the exception of those of sodium and calcium, with separation of the corresponding oxyds and formation of cuprous chlorid. In the case of zinc and manganese, insoluble oxychlorids of these metals are formed at the same time. These reactions require further study, and the same may be said of the cupric and cobaltic chlorids with cuprous oxyd. I have, however, partially investigated the behavior of cuprous oxyd with magnesian and ferrous chlorids, and obtained the results about to be described.

§ 3. The cuprous oxyd for these experiments was prepared by gently heating a solution of sulphate of copper mixed with cane sugar and an excess of caustic soda, until the whole of the copper was thrown down as a bright dense cinnabar-red powder

which was carefully washed and dried. A concentrated solution of chlorid of magnesium dissolves this oxyd in the cold, and more readily when heated, with separation of hydrated oxyd of magnesium and cuprous chlorid, which latter is held in solution by the excess of magnesian chlorid. By filtering the liquid while hot, and washing with a strong solution of chlorid of sodium, the hydrate of magnesia may be separated, and the dissolved copper subsequently precipitated by metallic iron from the colorless filtrate, ferrous chlorid being formed. Experiment shows that the reaction between the red oxyd of copper and chlorid of magnesium may be represented as follows:
$$\text{Cu}_2\text{O} + \text{MgCl} = \text{Cu}_2\text{Cl} + \text{MgO}.$$

§ 4. A solution of magnesian chlorid nearly saturated when hot with cuprous oxyd, and allowed to cool in contact with the precipitated magnesian hydrate, deposits a portion of orange colored oxyd, or perhaps an oxychlorid, which disappears as often as the solution is heated. The solid cuprous chlorid is moreover decomposed when digested with water and magnesia, hydrated cuprous oxyd and magnesian chlorid being formed. The double chlorid of cuprous and magnesium is however stable, even in the cold, in presence of magnesian hydrate, provided a considerable excess of magnesian chlorid be present. From a filtered solution of cuprous oxyd in chlorid of magnesium water precipitates a large portion of the cuprous chlorid, in this case colored orange-yellow from adhering oxyd, due to the reaction of a little magnesia, which remains dissolved or suspended in the concentrated solution even after filtration. A solution of magnesian chlorid of specific gravity 1.23, retains in solution at 12° Centigrade, about 7.10 per cent of cuprous chlorid. A solution of magnesian sulphate with chlorid of sodium may be employed to dissolve cuprous oxyd. This, like all similar solutions of cuprous chlorid, rapidly absorbs oxygen from the air and deposits a pale green cupric oxychlorid.

§ 5. With ferrous chlorid and cuprous oxyd it might be expected, from analogy with the magnesian salt, that we should obtain cuprous chlorid and ferrous oxyd, but the reaction is complicated by the tendency of the latter to pass to the state of ferric oxyd. When ferrous chlorid in solution with chlorid of sodium is heated with a sufficient quantity of cuprous oxyd, the whole of the iron is precipitated as ferric oxyd, mingled with metallic copper, while cuprous chlorid remains in solution. Experiments made with an excess of ferrous chlorid show that one third of the copper is reduced, while two thirds are dissolved as dichlorid. This reduction may be effected directly by ferrous oxyd; if to a solution of cuprous chlorid in chlorid of sodium, we add hydrated ferrous oxyd recently precipitated by an alkaline base and still suspended in the liquid, it is at once

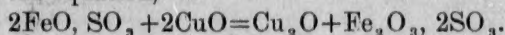
converted into ferric oxyd, with precipitation of metallic copper. The first stage in the action of ferrous chlorid on cuprous oxyd may be represented as similar to that of magnesian chlorid: $\text{Cu}_2\text{O} + \text{FeCl} = \text{Cu}_2\text{Cl} + \text{FeO}$. In the second stage $\text{Cu}_2\text{Cl} + 3\text{FeO} = \text{Cu}_2 + \text{FeCl} + \text{Fe}_2\text{O}_3$. It follows from this that one-third of the cuprous chlorid formed in the first stage is reduced to the metallic state, and the final result may be represented as follows: $3\text{Cu}_2\text{O} + 2\text{FeCl} = 2\text{Cu}_2\text{Cl} + 2\text{Cu} + \text{Fe}_2\text{O}_3$.

A similar result is obtained if ferrous chlorid is added to an unfiltered solution of cuprous oxyd in chlorid of magnesium. The suspended hydrate of magnesia in this case liberates an equivalent of ferrous oxyd, which reduces to the metallic state one-third of the dissolved cuprous chlorid, in accordance with the second reaction given above.

§ 6. The reducing power of ferrous oxyd is also shown with cupric chlorid, which is at once converted by it into cuprous chlorid in accordance with the equation, $2\text{CuCl} + 3\text{FeO} = \text{Cu}_2\text{Cl} + \text{FeCl} + \text{Fe}_2\text{O}_3$. The further action of ferrous oxyd will, as we have seen, reduce the cuprous chlorid to the metallic state: in fact, $2\text{CuCl} + 6\text{FeO} = 2\text{Cu} + 2\text{FeCl} + 2\text{Fe}_2\text{O}_3$. If recently precipitated hydrated ferrous oxyd or ferrous carbonate be added to a solution of cupric chlorid in the proportions indicated by the last equation, the whole of the copper is separated in the metallic state, mingled with ferric oxyd, while ferrous chlorid is found in solution. The reaction with ferrous carbonate, which requires a gentle heat, is accompanied by a violent disengagement of carbonic acid gas. This experiment is best made by dissolving in water ferrous sulphate and sodic carbonate or sodic hydrate in the proportions required, and adding thereto a solution holding the proper amount of cupric chlorid. Under certain conditions the cuprous precipitate is brownish-black in color, like that obtained by heating ferrous chlorid with cuprous oxyd, but more generally it is of a bright red color, and often coats the glass with a mirror-like film. A warm solution of cupric chlorid with chlorid of sodium at once converts the metallic copper of the precipitate into cuprous chlorid, which is dissolved, leaving behind only hydrated ferric oxyd. When a solution of ferrous chlorid with chlorid of ammonium and excess of ammonia is added to a solution of a copper salt the precipitated films of metallic copper sometimes possess considerable brilliancy and show a bluish translucency. It is to be remarked that although the cupreous precipitate thus obtained is bright red in color, that which is produced by boiling cuprous oxyd with ferrous chlorid is nearly black.

§ 7. It was long since shown by Levol that hydrated ferrous oxyd will reduce cupric to cuprous oxyd, and this, as we have already seen, can separate from its combinations ferrous oxyd,

whose reducing power may be still further exerted upon the cuprous combination thus formed. These facts serve to explain the results obtained by E. Braun (*Zeitschr. Chem.*, 1867, p. 568, cited in *Jahresbericht* for 1867), which were not known to me at the time of making these experiments. He found that by digesting cupric hydrate or cupric carbonate with ferrous sulphate in solution there was obtained a reddish mixture of basic ferric sulphate with cuprous oxyd, formed apparently in accordance with the equation,



This, when boiled with a further portion of ferrous sulphate, became black in color, and from the small amount of oxygen present was supposed to contain metallic copper. By adding a large excess of carbonate of ammonia to a mixture of ferrous and cupric sulphates, Braun succeeded in obtaining solutions in which all the copper was present in a cuprous form, and even in reducing portions of it to the metallic state, a process which we have seen is complete when the requisite amount of ferrous oxyd is brought in contact with the chlorids of copper.

§ 8. In this Journal for March, 1867, page 308, I described briefly the reaction between cupric oxyd and ferrous chlorid, according to the equation, $3\text{CuO} + 2\text{FeCl} = \text{Fe}_2\text{O}_3 + \text{Cu}_2\text{Cl} + \text{CuCl}$. I was not then aware that the same had been shown by Meyer (*Berg. und Hutt. Zeit.*, 1862, 182, cited by Kerl).^{*} Further studies of this reaction have given me interesting results. The black oxyd of copper, even after ignition, is attacked by ferrous chlorid in the cold, but the insolubility of the resulting cuprous chlorid retards the action. If however the ferrous chlorid be mingled with a strong solution of chlorid of sodium, and heat applied, the cuprous chlorid is readily dissolved, and the reaction is rapid and complete, the whole of the iron separating as a bulky reddish-brown precipitate, provided three equivalents of cupric oxyd have been taken for two of ferrous chlorid. The greenish solution thus obtained readily dissolves precipitated metallic copper, in virtue of the cupric chlorid which it contains, and, unless a large excess of chlorid of sodium be present, deposits white crystalline cuprous chlorid by cooling or by dilution. When digested at a temperature of 50° Centigrade with carbonate of lime, the greenish solution deposits one-third of its copper as a pale green insoluble cupric hydro-carbonate, while the colorless filtrate retains the remaining two-thirds in the form of cuprous chlorid. If a solution of ferrous chlorid with chlorid of sodium is digested with a sufficient excess of cupric oxyd the cupric chlorid formed unites with the latter to form an insoluble cupric oxychlorid, and only cuprous chlorid remains in solution.

^{*} *Metall. Huttenkunde*, xi, 588.





§ 9. For the ferrous chlorid in the experiments in § 5 and § 8, a solution of ferrous sulphate with chlorid of sodium may be substituted. When cupric oxyd is heated with an excess of ferrous chlorid, a small portion of ferric oxychlorid is produced. The red-brown precipitate may be washed free from cupric, cuprous and ferrous chlorids by a strong solution of chlorid of sodium, but will then yield to pure water a portion of soluble ferric oxychlorid. By careful desiccation in a water-bath and subsequent washing with dilute alcohol the ferric precipitate may be obtained free from chlorid of sodium, and completely insoluble in water; but its composition appears to be variable. Of two preparations the first contained one equivalent of chlorine for eleven, and the second, one for twenty equivalents of iron. In another experiment where fine oxyd of copper from the calcination of malachite was dissolved in an excess of a mixture of ferrous sulphate and chlorid of sodium at a boiling heat, it was found that for thirty equivalents of copper dissolved there were precipitated twenty-one equivalents of iron, instead of twenty as required by the formula given in § 8; the additional equivalent being separated as ferric chlorid in union with the ferric oxyd. The production of a small and variable amount of ferric chlorid in the above conditions is apparently due to a secondary reaction between cupric and ferrous chlorids in the presence of ferric oxyd; $2\text{CuCl} + 2\text{FeCl} = \text{Cu}_2\text{Cl} + \text{Fe}_2\text{Cl}_3$. This point however requires further investigation.

§ 10. The facility with which cupric chlorid parts with one-half of its chlorine and passes into the more stable cuprous compound is shown by its well known power to chloridize not only metallic copper, but metallic silver and even sulphid of silver. Its action on cuprous sulphid is not less remarkable. A strong solution of cupric chlorid mingled with chlorid of sodium rapidly attacks pulverized copper-glance, even in the cold, sulphur being separated and cuprous chlorid formed; $2\text{CuCl} + \text{Cu}_2\text{S} = 2\text{Cu}_2\text{Cl} + \text{S}$. Chalcopyrite, on the contrary, is but slightly acted upon by such a solution, which, however, slowly takes up a portion of iron, forming ferrous chlorid with a corresponding amount of cuprous chlorid.